REMARKS

Applicants respectfully request reconsideration of the present application in view of the foregoing amendments and in view of the reasons that follow. With this amendment, no claims have been amended, no claims have been cancelled, and no claims have been added. A detailed listing of all claims that are, or were, in the application, irrespective of whether the claim(s) remain under examination in the application, is presented, with an appropriate defined status identifier. Thus, claims 1, 10-22, 31-40, and 56-66 remain pending in the application, with claims 55, 58-60, and 63 having been withdrawn.

Claim Rejections - 35 USC § 112

Claims 1, 10-22, 31-40, 56-57, 61-62, and 64-66 were rejected under 35 U.S.C. 112, second paragraph, as being indefinite. Specifically, the in paragraph 3 of the Action, Examiner alleges the feature "wherein the porous membrane is a sensor exhibiting sensing characteristics causing a change in at least one of an optical and electrical characteristic in response to exposure to a targeted fluid or reaction" is unclear. Applicants respectfully traverse the rejection.

This feature is clear on its face. It means that the porous membrane having the porous silicon membrane itself is a sensor in the micro-fluidic devices of claims 1 and 22.

The Examiner states that "[i]t is not clear what Applicant means by the phrase 'sensing characteristics'." See paragraph 3 of the Action. The phrase "sensing characteristics" means properties to sense "a change in at least one of an optical and electrical characteristic in response to exposure to a targeted fluid or reaction" as recited in claims 1 and 23.

The Examiner further states, "Nor does the specification clarify the matter [i.e., sensing characteristics]." See paragraph 3 of the Action. The phrase "sensing characteristics" is clarified in

the specification and needs to be viewed in the context of the specification. Paragraph [0029] of the specification states "[a]t the cross-channel area 108, a portion of the sample fluid 126b will flow through or attach to the porous membrane 110, causing a reaction, such as a potential change in an optical and/or electrical characteristic of the porous membrane 110. Such a characteristic change may be measured in the manners described below." Examples of numerous measurement techniques and/or properties for which measurement is described follow in the specification. Examples include, but are not limited to: "The field force/gradient may an electric field, magnetic field, acoustic wave, ultrasounds, light with specific wavelengths and other fields capable of interacting with the molecules of interest" [0032], "Generally, such PSi or PPSi sensor mechanisms may include but are not limited to optical interferometric reflectivity, capacitance modulation, photoluminescence, optical form birefringence, acoustic, *etc.*" [0039], The light emitted and/or scattered may be detected such as absorption, luminescence (fluorescence and phosphorescence), vibrational (infra-red, Raman, resonance Raman, etc.), SPR (surface plasmon resonance), etc." [0041], and "In one embodiment, the optical detector 302 comprises a detector suitable for laser interferometry. Other typical optical detectors include, but are not limited to, avalanche photodiodes, various photosensors, and other devices used to measure wavelength, phase shift, and or optical energy/power." [0042]. That is, the specification teaches a large selection of "optical and electrical characteristics." Applicants submit that one of ordinary skill in the art reading the specification would not find the phrase "wherein the porous membrane is a sensor exhibiting sensing characteristics causing a change in at least one of an optical and electrical characteristic in response to exposure to a targeted fluid or reaction" unclear.

The Examiner has also stated that "[i]t is not clear how the use of a semiconductor material such as silicon provides a 'sensing characteristic'." See paragraph 3 of the Action. The reason why a semiconductor material such as a porous silicon membrane provides a "sensing characteristic causing a change in at least one of an optical and electrical characteristic in response to exposure to a targeted fluid or reaction," as recited in claims 1 and 23, is that porous silicon is a material which is both semiconducting and provides luminescence. *See*, "Porous Silicon as a Biomaterial" at http://www.azom.com/details.asp?ArticleID=529 attached herewith. Hence, porous silicon itself can be either an electrical or optical sensor capable of sensing "at least one of an optical and electrical characteristic in response to exposure to a targeted fluid or reaction," as recited in claims 1 and 22.

Applicants respectfully request withdrawal of the rejection.

Claim Rejections - 35 USC § 103

Claims 1, 10-22, 31-40, 56-57,61-62, and 64-66 were rejected under 35 U.S.C. 103(a) as being unpatentable over US Patent Pub. No. 2003/0136679 to Bohn et al., in view of US Patent Pub No. 2003/0148524 to Zimmermann et al. Applicants respectfully traverse the rejection.

In the rejection, the Examiner makes the following statements:

A. The Bohn device also includes a porous membrane 22 integral with the substrates 24, 26 (claim 18) and separating the source fluid flow channel from the target fluid flow channel in the cross-channel area. The porous membrane 22 is a sensor exhibiting sensing characteristics causing a change in an electrical characteristic in response to exposure to a targeted fluid or reaction. That is, Bohn teaches the interior surface 60 of each pore 42 may be coated with a coating 62 (see Fig. 3), so that molecules passing through the pore are likely to contact coating. (Page 4, lines 14-20).

B. It is noted that Applicant teaches the addition of a sensor layer as an alternative to use of a base silicon substrate material (e.g., PSi or PPSi), see paragraph [0039] of the specification. (Page 5, lines 3-5).

C. Zimmermann teaches the carrier member can be formed of a membrane comprising polycarbonate or silicon nitride (see paragraph [0028]). Note the claims recite the porous membrane "comprising" porous silicon membrane. "Comprising" is a term of art used in claim language which means that the named elements are essential, but other elements may be added and still form a construct within the scope of the claim. Thus, porous silicon nitride membrane reads on the "porous silicon membrane". (Page 5, line 22 to page 6, line 4).

That is, in statement A the Examiner argues that Bohn teaches a device with a porous membrane. Applicants agree. The Examiner also argues that the porous membrane of Bohn could act as a sensor if the pores are coated with a coating that is capable of detecting a change in an electrical characteristic. Applicants also agree. Then, citing Applicants' own specification in statement B, the Examiner suggests that it would have been obvious to modify the coated porous polycarbonate membrane (PCTE) of Bohn with an uncoated porous silicon membrane because Applicants teach that the addition of a sensor layer is an alternative to an uncoated porous silicon membrane. It is here that Applicants and the Examiner must part ways.

Applicants do not agree with the Examiner it would have been obvious to modify the coated porous polycarbonate membrane (PCTE) of Bohn with an uncoated porous silicon membrane for the following reason. The factual basis for the Examiner to arrive at this conclusion stems from hindsight gained from Applicants' own invention. "Impermissible hindsight must be avoided and the legal conclusion must be reached on the basis of the facts gleaned ***from the prior art***." *See*, MPEP 2142 (Emphasis added). Indeed, Applicants note that MPEP 2142 specifically prohibits the examiner from using teachings only found in Applicants own specification - "Knowledge of

applicant's disclosure must be put aside in reaching this [obviousness] determination." Applicants teach two distinct embodiments in the present application. One embodiment comprises a porous membrane with a sensor layer. The other comprises a membrane made of a material that itself can act as a sensor without the need of a sensor layer. That these two embodiments are alternatives is ***only*** taught in Applicants' specification, and was first recognized by Applicants themselves. Indeed, the Examiner has not provided any teaching, reference or reasoning with some rational underpinning to support the legal conclusion of obviousness, ***other than Applicants' specification***, which would suggest that an uncoated semiconducting porous silicon membrane is an alternative to the metal coated porous membrane of Bohn et al. Applicants note that even under the KSR standard for obviousness, "[r]ejections on obviousness grounds cannot be sustained by mere conclusory statements; instead, there must be some articulated reasoning with some rational underpinning to support the legal conclusion of obviousness." *KSR Int'l Co. v. Teleflex Inc.*, No. 04-1350, slip op. at 11 (U.S. April 30, 2007)(citing In re Kahn, 441 F.3d 977, 988 (Fed. Cir. 2006)). For at least this reason, independent claims 1 and 22 and their dependent claims would not have been obvious to one of ordinary skill in the art at the time of the invention.

Regarding statement C above, Applicants agree that the transition phrase "comprising" is open ended. Claims 1 and 22 recite "the porous membrane comprises a porous silicon membrane." In order for the silicon nitride of Zimmermann et al. to be within the scope of the limitation "the porous membrane comprises a porous silicon membrane," the silicon nitride of Zimmermann et al. ***must at least contain*** "a porous silicon membrane." Applicants respectfully submit that the silicon nitride of Zimmermann et al. neither contains nor is equivalent to "a porous silicon membrane."

Please note that "porous silicon" is a term of art and has been defined as "***a form of the chemical element silicon*** which has an introduced nanoporous holes in its microstructure … ." *See*, "Porous silicon" Wikipedia entry at http://en.wikipedia.org/wiki/Porous_silicon attached herewith; emphasis added.

Silicon nitride, in contrast, is "(Si_3N_4) is a hard, solid substance" that "[i]n microelectronics, … is usually used either as an insulator layer to electrically isolate different structures or as an etch mask in bulk micromachining." *See*, "Silicon Nitride" Wikipedia entry at http://en.wikipedia.org/wiki/Silicon_nitride attached herewith. Simply, porous silicon and porous silicon nitride are not the same. Furthermore, silicon nitride does not necessarily contain ***elemental*** silicon.

Foremost, nowhere does Zimmermann et al. disclose that the silicon nitride disclosed therein contains any "porous silicon" that is "***a form of the chemical element silicon*** which has an introduced nanoporous holes in its microstructure."

Also, the silicon nitride of Zimmermann et al. is not equivalent to "a porous silicon membrane." To argue that silicon nitride is equivalent to elemental silicon just because both materials contain silicon, would amount to arguing that carbon dioxide is equivalent to elemental carbon just because both contain carbon. Clearly this is not correct.

Furthermore, because silicon nitride is insulating, the silicon nitride of Zimmermann et al. is ***not*** capable of performing as "a sensor exhibiting sensing characteristics causing a change in at least one of an optical and electrical characteristic in response to exposure to a targeted fluid or reaction" as recited in independent claims 1 and 22. Applicants respectfully submit that the Examiner should ***not*** ignore the functional language that "the porous membrane is ***a sensor exhibiting sensing***

characteristics causing a change in at least one of an optical and electrical characteristic in response to exposure to a targeted fluid or reaction" (emphasis added) as recited in independent claims 1 and 22. See MPEP 2173.05(g), which states:

> A functional limitation is an attempt to define something by what it does, rather than by what it is (e.g., as evidenced by its specific structure or specific ingredients). There is nothing inherently wrong with defining some part of an invention in functional terms. Functional language does not, in and of itself, render a claim improper. *In re Swinehart*, 439 F.2d 210, 169 USPQ 226 (CCPA 1971).
>
> ***A functional limitation must be evaluated and considered, just like any other limitation of the claim, for what it fairly conveys to a person of ordinary skill in the pertinent art in the context in which it is used.*** A functional limitation is often used in association with an element, ingredient, or step of a process to define a particular capability or purpose that is served by the recited element, ingredient or step. [Emphasis added.]

Applicants therefore respectfully request withdrawal of the rejection.

In view of the above amendment, Applicants believe the pending application is in condition for allowance.

Dated: December 9, 2008

Respectfully submitted,

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- ATTACHMENTS

Silicon nitride

From Wikipedia, the free encyclopedia

Silicon nitride (Si_3N_4) is a hard, solid substance. It is the main component in silicon nitride ceramics, which have relatively good shock resistance and other mechanical and thermal properties as compared to other ceramics.

Silicon nitride	
Identifiers	
CAS number	12033-89-5
Properties	
Molecular formula	N_4Si_3
Molar mass	140.28 g mol^{-1}
Appearance	grey, odorless powder
Density	3.44 g/cm^3, solid
Melting point	1900 °C, 2173 K, 3452 °F (decomposes)
Hazards	
EU classification	not listed
Except where noted otherwise, data are given for materials in their standard state (at 25 °C, 100 kPa) Infobox references	

Contents

- 1 Synthesis
- 2 Crystal Structure
- 3 Applications
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Synthesis

Silicon nitride can be obtained by direct reaction between silicon and nitrogen at high temperatures. Electronic-grade silicon nitride is usually formed using chemical vapor deposition (CVD), or one of its variants, such as plasma-enhanced chemical vapor deposition (PECVD). Silicon nitride nanowires can also be produced by sol-gel method.[1]

Natural existence of silicon nitride is restricted to meteorites, where it very rarely occurs as mineral nierite.

Crystal Structure

There exist 3 crystallographic structures of silicon nitride (Si_3N_4), designated as α, β and γ phases. The α and β phases are the most common forms of Si_3N_4, and can be produced under normal pressure condition. The γ phase can only be synthesized under high pressures and temperatures and has a hardness of 35 GPa[2].

Pictures of crystallographic structure of the α- and β- Si_3N_4 can be found here[3], and properties of the γ phase in this reference.[4]

α- and β-Si_3N_4 have hexagonal structures, which are built up by corner-sharing SiN_4 tetrahedra. They can be regarded as consisting of layers of silicon and nitrogen atoms in the sequence ABAB... or ABCDABCD... in β-Si_3N_4 and α-Si_3N_4, respectively. The AB layer is the same in the α and β phases, and the CD layer in the α phase is related to AB by a c-glide plane. The Si_3N_4 tetrahedra in β-Si_3N_4 are interconnected in such a way that tunnels are formed, running parallel! with the c axis of the unit cell. Due to the c-glide plane that relates AB to CD, the α structure contains cavities instead of tunnels. The cubic γ-Si_3N_4 is often designated as c modification in the literature, in analogy with the cubic modification of boron nitride (c-BN). It has a spinel-type structure in which two silicon atoms each coordinate six nitrogen atoms octahedrally, and one silicon atom coordinates four nitrogen atoms tetrahedrally.[5]

Applications

Silicon nitride ceramics have relatively good shock resistance compared to other ceramics. Therefore, ball bearings made of silicon nitride ceramic are used in performance bearings. Silicon nitride ball bearings are harder than metal which reduces contact with the bearing track. This results in less friction, less wasted energy and higher speed. They are also much lighter and more durable than metal bearings under steady loads, the downside being their higher cost. Silicon nitride ball bearings can be found in high end automotive bearings, industrial bearings, wind turbines and even sometimes in high-end skateboards.

Silicon nitride is also used as an ignition source for domestic gas appliances, hot surface ignition.

In microelectronics, silicon nitride is usually used either as an insulator layer to electrically isolate different structures or as an etch mask in bulk micromachining. As a passivation layer for microchips, it is superior to silicon dioxide, as it is a significantly better diffusion barrier against water molecules and sodium ions, two major sources of corrosion and instability in microelectronics. It is also used as a dielectric between polysilicon layers in capacitors in analog chips.

Bulk, monolithic silicon nitride is used as a material for cutting tools, due to its hardness, thermal stability, and resistance to wear. It is especially recommended for high speed machining of cast iron. For machining of steel, it is usually coated by titanium nitride (usually by CVD) for increased chemical resistance.

Further reading

- Topical review Sci. Technol. Adv. Mater. 9 (2008) 033001 (47pp) ***free download***
- "Fabrication of silicon nitride nanoceramics—Powder preparation and sintering: A review" Sci. Technol. Adv. Mater. 8 (2007) 635 ***free download***
- Silicon Nitride – An Overview
- V.I. Belyi and L.L. Vasilyeva "Silicon Nitride in Electronics" Elsevier, Nederlands, 1988, ISBN-10: 0444426892

References

1. ^ Sci. Technol. Adv. Mater. 9 (2008) 015002 ***free download***
2. ^ "Hardness and thermal stability of cubic silicon nitride" *J. Phys.: Condens. Matter* 13, 22, L515 (2001)
3. ^ Crystal structures of Si3N4
4. ^ Properties of gamma-Si3N4
5. ^ Spark Plasma Sintering of Si3N4-Based Ceramics

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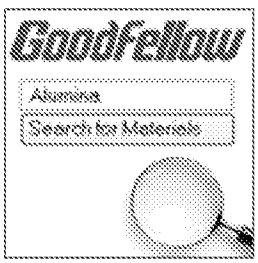

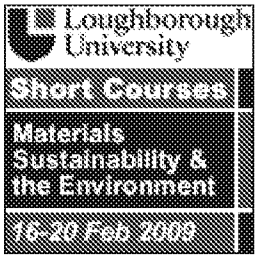

Porous Silicon as a Biomaterial

Topics Covered
Background
- Silicon as a Biomaterial
- Semiconductors

Porous Silicon
- Production of Porous Silicon
- Characteristics of Porous Silicon

Biocompatibility
- Bioactive Biomaterials
- Toxicity

The Future

Background

Science fiction has long predicted the union of humans and computers. Many children in the 1960s and 1970s were avid fans of 'The Six Million Dollar Man' TV

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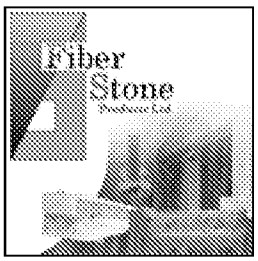

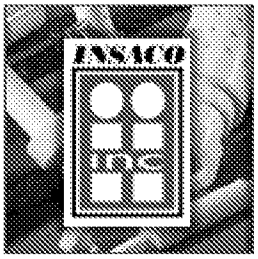

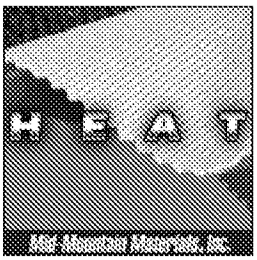
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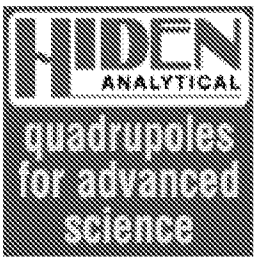
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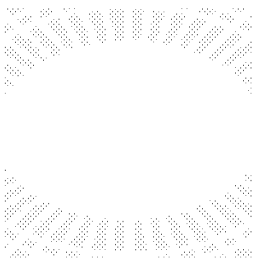

sensing devices that need to be linked to the biological system.

Semiconductors

Such devices would almost certainly use semiconductor-based technologies. The two basic types of components built with semiconductor materials are transistors and laser diodes. Transistors are silicon-based and laser diodes are gallium arsenide-based. From an electronics point of view, it would better to make transistors and laser diodes from the same material. From the point of view of developing biologically compatible devices, the need for new materials is more pressing. Gallium arsenide is toxic to biological systems and although the toxicity of bulk silicon is unproven, the material is nonetheless poorly biocompatible.

Porous Silicon

The search for an efficient, luminescent semiconductor that could play the roles of both laser diode and transistor took a big step forward when porous silicon demonstrated these properties. The material is also biocompatible, and so it is hoped that the use of porous silicon will speed up the development of biologically interfaced devices. The material could prove to be the bridge that allows signals and information to be transmitted between a semiconductor device and a biological system.

Production of Porous Silicon

Porous silicon was discovered by accident. It was produced by non-uniform etching during the electropolishing of silicon with an electrolyte

containing hydrofluoric acid. The etching resulted in a system of disordered pores with nanocrystals remaining in the inter-pore regions. Porous silicon is still manufactured by electrochemical etching of silicon in hydrofluoric acid (HF) solutions. Aqueous HF is unsuitable for the etching process because the silicon surface is hydrophobic. The porous layer can be made more structurally uniform if an ethanoic solution is used - this increases the wettability of the silicon and allows better surface penetration by the acid. Ethanoic etch solutions also reduce the formation of hydrogen gas bubbles as ethanol acts as a surfactant and prevents bubbles sticking to the silicon surface.

Developing an etching cell to allow the maximum control of the reproducibility, porosity and thickness of porous silicon is a major concern of researchers in the field. However, understanding how to control PS morphology is extremely difficult owing to the large number of contributing factors. This means that PS is an inherently disordered material with poorly specified properties. Its luminescent properties are explained by a quantum confinement model. This suggests that the enhanced and blue-shifted luminescent emissions result from excitation recombination in quantum confined nano-structures within the PS skeleton.

Characteristics of Porous Silicon

PS is classified as microporous (with a pore size greater than 50nm), mesoporous (pore size of 5-

50nm) or nanoporous (pore size less than 5nm). Transmission electron microscopy (TEM) is used to directly image PS layers and accurate pore size distribution information is obtained from gas adsorption isotherms generated at low temperature. The material is usually mono-crystalline but evidence for amorphous regions has been found using x-ray scattering, x-ray absorption fine structure, Raman spectroscopy and electron microscopy. These techniques show that the amount of amorphous layer varies with oxidation, ageing and post-anodisation treatment, yet the gross microscopic structure remains that of silicon nanocrystals embedded in an amorphous web-like matrix.

The silicon nanocrystals in PS that emits visible light vary in size from 10-15Å. Raman spectroscopy gives indirect information about the microstructure of PS and has shown that the nanocrystals alter the selection rules relating to the interaction of optical phonons with incident photons. This broadens the associated Raman peak and gives rise to the photoluminescent properties seen in porous but not bulk silicon.

The internal surface area of a PS layer varies from 200-600ml per square centimetre of external surface. The surface contains impurities from the air and the etching process that affect the optical and electrical properties of the material and could potentially affect biological systems such as living cells in contact with the surface. Common impurities include hydrogen, fluorine and oxygen. The levels of

hydrogen and fluorine decrease over time as they are replaced with hydroxyl groups on hydrolysis by atmospheric water. As much as 1% oxygen is normally adsorbed within minutes of air drying. Over a few days Si-O-Si, O-Si-H and O_3-Si-H groups are formed. These oxides at the PS surface are thought to play a crucial role in the biocompatibility of the material.

Biocompatibility

Biocompatibility is the ability of a material to interface with a natural substance without provoking a natural response. The human body typically responds to contact with synthetic materials by depositing proteins and cells from body fluids at the surface of the materials. This can cause infection and biological rejection of devices manufactured from non-compatible materials. The majority of today's medical devices are made from materials such as PVC, polypropylene, polycarbonate, fluorinated plastics and stainless steel. These materials are 'tolerated' by the human body and are described as 'bioinert'.

Bioactive Biomaterials

An effective biomaterial must bond to living tissue - in other words, it has to be 'bioactive'. The success of any medical implant depends on the behaviour of cells in the vicinity of the interface between the host and the biomaterial used in the device. All biomaterials have morphological, chemical and electrical surface characteristics that influence the response of cells to the implant. The initial event is the adsorption of a layer of

protein on to the biomaterial. Generally, uncontrolled adsorption of a lot of proteins is undesirable in a biocompatible material.

The absorption of human serum albumin (HSA) and fibrinogen has been measured for porous silicon. Hydration of the porous surface significantly decreases the adsorption of HSA but increases the amount deeper in the porous film. Hydration does not affect the adsorption of fibrinogen, a protein essential in blood clotting processes. Another important test is the in vitro deposition of hydroxyapatite onto the surface of a biomaterial from a simulated body fluid. This has become a standard indicator of potential bioactivity for materials for bone implantation. Porous silicon is reactive towards hydroxyapatite formation - this was the first indication of its potential as a biomaterial.

Toxicity

The possibility of toxic effects from porous silicon also needs to be considered. Silicon is essential in biological systems as it affects both morphological development and metabolic processes. However, despite its importance little is known about the biological processes that handle silicon at the molecular level. What is known is that silicon-induced toxicity may occur if a system is exposed to more silicon than is needed physiologically.

Many studies have been carried out on the possible toxicity of implanted silicone, but there are few positive reports about the toxicity of silicon or its compounds. At Leicester we have demonstrated that cells

seeded into a plate containing silicon substrates grow to form a complete continuous sheet -confluence - on the plastic surrounding the silicon material in the predicted time. We have also shown that it is possible to culture cells on a PS substrate and that these cells are viable in terms of structure and metabolism. The PS wafers were not fatally toxic to the cells over a period of 10 days and presented an acceptable surface for growth. The effect of any substances released from the PS substrates was minimal. However, these results must be quantified, and further studies are in progress to confirm the non-toxicity of PS.

The Future

If PS proves to be non-toxic then nanoporous silicon will offer a distinct advantage over other semiconductors such as gallium arsenide and indium arsenide. Arsenic and indium induce apoptosis (programmed cell death) in rat cells in vitro. In addition, cells are sensitive to topological, chemical and electrical properties of substrates on which they are grown. Cells cultivated on microstructures made by semiconductor technology grow normally on silicon surfaces covered with microelectrode arrays, as well as on microperforated silicon membranes with square pores made by anisotropic etching. The pores have edges 5, 10 or 20 µm long at the top and 1.2, 6.2 or 16.2µm at the bottom. The cells spread over the 5 and 10 µm pores, but mostly failed to cover the 20 µm ones. The size of the pores in PS therefore does not present a problem to cell growth.

The ability to culture mammalian cells directly onto PS, coupled with the material's apparent lack of toxicity, offers exciting possibilities for the future of biologically interfaced sensing. This could involve the development of biologically interfaced neural networks, or electronic sensing with signals being directly sent from a living system to a PS device. Another benefit is that the optical and optoelectronic properties of PS could allow it to be linked to a data logger by optical fibres. This would remove the risk of electromagnetic forces influencing the responses of cells.

In this way, porous silicon has the potential to produce devices for replacing damaged tissues in the ear, eye, skin or nasal cavity. Such devices could, for example, receive optical information and convert this to a biological signal that would be passed into neural tissue as a substitute 'sight' sensation. Alternatively, PS could be used to build environmental or pharmaceutical sensing systems. Optical signals to and from the material could be used to sense wavelength shifts, which would correspond to changes in attached cells caused by the presence of chemicals or drugs.

Primary author: Lorraine Buckberry and Sue Bayliss
Source: Materials World. Vol. 7 no. 4 pp. 213-15, April 1999.

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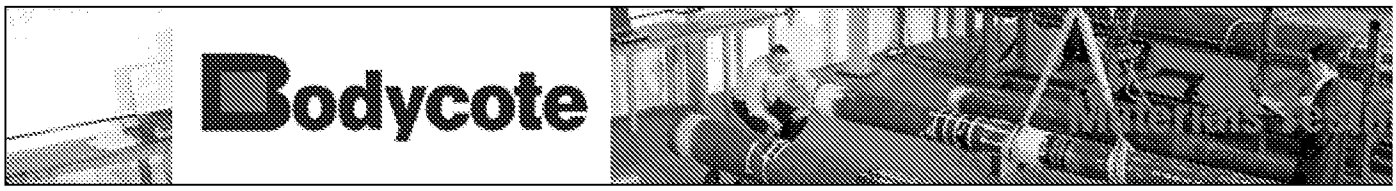

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Porous silicon

From Wikipedia, the free encyclopedia

Porous Silicon (pSi) is a form of the chemical element silicon which has an introduced nanoporous holes in its microstructure, rendering a large surface to volume ratio in the order of $500m^2/cm^3$.

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History

Porous silicon was first discovered by accident in 1956 by Arthur Uhlir Jr. and Ingeborg at the Bell laboratories in US. At the time, Ulhir and Ingeborg were in the process of developing a technique for polishing and shaping the surfaces of silicon and germanium. However, it was found that under several conditions a crude product in the form of thick black, red or brown film were formed on the surface of the material. At the time, the findings were not taken further and were only mentioned in Bell's labs technical notes.[1]

Despite the discovery of porous silicon in the 1950's, the scientific community was not interested in porous silicon until the late 1980's. At the time, Leigh Canham – whilst working at the Defence Research Energy in England – reasoned that the porous silicon may display quantum confinement effects [2]. The intuition was followed by successful lab results published in the 1990. In the published experiment, it was revealed that silicon wafers can emit light if subjected to electrochemical and chemical dissolution.

The published result stimulated the interest of the scientific community in its non-linear optical and electrical properties. The growing interest was evidenced in the number of published work concerning the properties and potential applications of porous silicon. In an article published in 2000, it was found that the number of published work grew exponentially in between 1991 and 1995[3]

In 2001, a team of scientists at the Technical University of Munich inadvertently discovered that hydrogenated porous silicon reacts explosively with oxygen at cryogenic temperatures, releasing several times as much energy as an equivalent amount of TNT, at a much greater speed (an abstract of the study can be found below).

Explosion occurs because the oxygen, which is in a liquid state at the necessary temperatures, is able to oxidize through the porous molecular structure of the silicon extremely rapidly, causing a very quick and efficient detonation. Although hydrogenated porous silicon would probably not be effective as a weapon, due to its functioning only at low temperatures, other uses are being explored for its explosive properties, such as providing thrust for satellites.

Fabrication of Porous Silicon

Fabrication of porous silicon may range from its initial formation through stain-etching or anodization cell, drying and storage of porous silicon and surface modification needed.

Formation of Porous Silicon by Anodization

One method of introducing pores in silicon is through the use of an anodization cell. A possible anodization cell employs platinum cathode and silicon wafer anode immersed in Hydrogen Fluoride (HF) electrolyte. Corrosion of the anode is produced by running electrical current through the cell. It is noted that the running of constant DC current is usually implemented to ensure steady tip-concentration of HF resulting in a more homogenous porosity layer although pulsed current is more appropriate for the formation of thick silicon wafers bigger than 50μm[4]

It was noted by Halimaoui that hydrogen evolution occurs during the formation of porous silicon.

> "When purely aqueous HF solutions are used for the PS formation, the hydrogen bubbles stick to the surface and induce lateral and in-depth inhomogeneity"

The hydrogen evolution is normally treated with absolute ethanol in concentration exceeding 15%. It was found that the introduction of ethanol eliminates hydrogen and ensures complete infiltration of HF solution within the pores. Subsequently, uniform distribution of porosity and thickness is improved.

Formation of Porous Silicon by Stain Etching

It is possible to obtain porous silicon through stain-etching with hydrofluoric acid, nitric acid and water. A publication in 1957 revealed that stain films can be grown in dilute solutions of nitric acid in concentrated hydrofluoric acid.[5] Porous silicon formation by stain-etching is particularly attractive because of its simplicity and the presence of readily available corrosive reagents; namely Hydrogen Nitride (HNO3) and Hydrogen Fluoride (HF). Furthermore, stain-etching is useful if one needs to produce a very thin porous Si films.[6] A publication in 1960 by R.J. Archer revealed that it is possible to create stain films as thin as 25Å through stain-etching with HF-HNO3 solution.

Drying of Porous Silicon

Porous silicon is systematically prone to presence of cracks when the water is evaporated. The cracks are particularly evident in thick or highly porous silicon layers.[7] The origin of the cracks has been attributed to the large capillary stress due to the minute size of the pores. In particular, it has been known that cracks will appear for porous silicon samples with thickness larger than a certain critical value. Bellet concluded that it was impossible to avoid cracking in thick porous silicon layers under normal evaporating conditions. Hence, several appropriate techniques have been developed to minimize the risk of cracks formed during drying.

Supercritical Drying

Supercritical drying is reputed to be the most efficient drying technique but is rather expensive and difficult to

implement. It was first implemented by Canham in 1994 and involves superheating the liquid pore above the critical point to avoid interfacial tension.

Freeze Drying
Freeze drying was first implemented by Gruning and Yelon in 1995. After the formation of porous silicon, the sample is frozen at a temperature of around -500F and sublimed under vacuum.

Pentane Drying
The technique uses pentane as the drying liquid instead of water. In doing so the capillary stress is reduced because pentane has a lower surface tension than water.

Slow Evaporation Rate
Slow evaporating technique can be implemented following the water or ethanol rinsing. It was found that slow evaporation decreased the trap density

Surface Modification of Porous Silicon

The surface of porous silicon may be modified to exhibit different properties. Often, freshly etched porous silicon may be unstable due to the rate of its oxidation by the atmosphere or unsuitable for cell attachment purposes. Therefore, it can be surface modified to improve stability and cell attachment

Surface Modification Improving Stability

Following the formation of porous silicon, its surface is covered with covalently bonded hydrogen. Although the hydrogen coated surface is sufficiently stable when exposed to inert atmosphere for a short period of time, prolonged exposure render the surface prone to oxidation by atmospheric oxygen. The oxidation promotes instability in the surface and is undesirable for many applications. Thus, several methods were developed to promote the surface stability of porous silicon.

An approach that can be taken is through thermal oxidation. The process involves heating the silicon to a temperature above 1000 C to promote full oxidation of silicon. The method reportedly produced samples with good stability to ageing and electronic surface passivation[8]

Porous silicon exhibits a high degree of biocompatibility. The large surface area enables bio-organic molecules to adhere well. It degrades to silicic acid, which causes no harm to the body. This has opened potential applications in medicine such as a framework of the growth of bone.

Surface Modification Improving Cell Adhesion

Surface modification can also affect properties that promote cell adhesion. One particular research in 2005 studied the mammalian cell adhesion on the modified surfaces of porous silicon. The research used rat PC12 cells and Human Lens Epithelial (HLE) cells cultured for four hours on the surface modified porous silicon. Cells were then stained with vital dye FDA and observed under fluorescence microscopy. The research concluded that 'amino silanisation and coating the pSi surface with collagen enhanced cell attachment and spreading'[9]

Classification of Porous Silicon

Porosity

'The porosity is defined as the fraction of void within the PS layer and can be determined easily by weight measurement'.[4] During formation of porous silicon layer through anodisation, the porosity of a wafer can be increased through increasing current density, decreasing HF concentration and thicker silicon layer. The porosity of porous silicon may range from 4% for macroporous layers to 95% for mesoporous layers. A study by Canham in 1995 found that 'a lum thick layer of high porosity silicon completely dissolved within a day of in-vitro exposure to a simulated body fluid'[10] It was also found that a silicon wafer with medium to low porosity displayed more stability. Hence, the porosity of porous silicon is varied depending on its potential application areas.

Pore Size

The porosity value of silicon is a macroscopic parameter and doesn't yield any information regarding the microstructure of the layer. It is proposed that the properties of a sample are more accurately predicted if the pore size and its distribution within the sample can be obtained. Therefore, porous silicon has been divided into three categories based on the size of its pores; macroporous, mesoporous, and microporous.

Type	Microporous	Mesoporous	Macroporous
Pore width (Nanometer)	less than 2	Between 2 and 50	Larger than 50

Key Characteristic of Porous Silicon

Highly Controllable Properties

Porous silicon studies conducted in 1995 showed that the behaviour of porous silicon can be altered in between 'bio-inert', 'bioactive' and 'resorbable' by varying the porosity of the silicon sample. [10]The in-vitro study used simulated body fluid containing ion concentration similar to the human blood and tested the activities of porous silicon sample when exposed to the fluids for prolonged period of time. It was found that high porosity mesoporous layers were completely removed by the simulated body fluids within a day. In contrast, low to medium porosity microporous layers displayed more stable configurations and induced hydroxyapatite growth.

Bioactive

The first sign of porous silicon as a bioactive material was found in 1995. In the conducted study, it was found that hydroxyapatite growth was occurring on porous silicon areas. It was then suggested by author L.T. Canham that 'hydrated microporous Si could be a bioactive form of the semiconductor and suggest that Si itself should be seriously considered for development as a material for widespread in vivo applications'[10] Another paper published the finding that porous silicon may be used a substrate for hydroxyapatite growth either by simple soaking process or laser-liquid-solid interaction process[11]

Since then, in-vitro studies have been conducted to evaluate the interaction of cells with porous silicon. One particular study in 1995 studied the interaction of B50 rat hippocampal cells with porous silicon and found that B50 cells have clear preference for adhesion to porous silicon over untreated surface. The study indicated that porous silicon can be suitable for cell culturing purposes and can be used to control cell growth pattern[12]

Non Toxic Waste Product

Another positive attribute of porous silicon is the degradation of porous silicon into monomeric silicic acid ($SiOH_4$). Silicic acid is reputed to be the most natural form of element in the environment and is readily

removed by kidneys.

The human blood plasma contains monomeric silicic acid at levels of less than 1mg Si/l, corresponding to the average dietary intake of 20-50mg/day. It was proposed that the small thickness of silicon coatings presents minimal risk to a toxic concentration being reached. The proposal was supported by an experiment involving volunteers and silicic-acid drinks. It was found that concentration of the acid rose only briefly above the normal 1mg Si/l level and was efficiently expelled by urine excretion[13]

See also

- Nanocrystalline silicon
- Silicon
- Porosity
- Quantum wire
- Etching (microfabrication)

External links

- Abstract of the study of porous silicon as an explosive

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